



Synthesis of Polypropylene/Poly(ethylene-co-propylene) In-situ Blends Using 5th Generation of Ziegler-Natta Catalyst

Mehrsa Emami^{1*}, Monirossadat Sadati², Farzin Hormozi¹,
Reza Mehtarani¹, and Ahmad Mirzaei¹

(1) Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, Iran
(2) Customer Oriented Research and Technology Department (C.O.R&T) of National Petrochemical Company, Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, Iran

Received 10 January 2007; accepted 22 August 2007

ABSTRACT

Polypropylene/poly(ethylene-co-propylene) in-reactor blends were synthesized by sequential multi-stage polymerization technique using fifth generation of Ziegler-Natta catalyst. Blends of isotactic polypropylene (iPP) (with a minimum isotacticity index (II) of 97.5%) and at least 12% ethylene/propylene copolymer were successfully synthesized. Experimental set-up and polymerization procedure are described in detail. Effect of external electron donor on catalyst behaviour was studied. The results showed that for the catalytic system investigated, using external electron donor causes a decrease in catalyst hydrogen response and productivity at both homo and copolymerization stages and an increase in the ratio between amorphous to crystalline ethylene-propylene copolymer of the blend. Furthermore, increasing the proportion of C₂ in the copolymerization stage leads to increase of both polymerization rates and the amount of ethylene/propylene rubber (EPR) in the blend.

Key Words:

synthesis;
polypropylene;
ethylene/propylene rubber;
in-situ blend.

INTRODUCTION

The application of isotactic polypropylene (iPP) as an engineering plastic is limited owing to its poor impact toughness in particular at the lower temperatures. An obvious way to alleviate this drawback is to create a mixed system containing a compatible elastomer such as ethylene/propylene rubber

(EPR) with the isotactic homopolymer (iPP). The iPP/EPR blends are called toughened or high-impact polypropylene which find wide application in consumer and automotive industry [1,2].

Developments achieved in the catalyst architecture and polymerization technologies, made possible

(*) To whom correspondence to be addressed.

E-mail: m.emami@ippi.ac.ir

the production of blends in-situ directly in the reactor [3-5]. Blends prepared by in-situ or in-reactor blending techniques have been proved to be superior with respect both in mechanical properties and production costs in comparison to iPP/EPR blends formed by mechanical blending [6,7]. A typical in-situ blend is prepared by sequential polymerization of propylene in the first step, followed by ethylene/propylene copolymerization in the second step. In this method, homopolymer matrix is obtained at the first stage followed by the second step to form elastomeric part of the product [1]. Many processes are developed to obtain multi-polymer alloys directly in the reactor, such as Spheripol, Catalloy and Spherizone. The Spheripol process is a two-stage hybrid process as it consists of bulk technology in the liquid monomer for production of homopolymer (or random copolymer) and the gas phase technology for the production of heterophasic copolymers [8]. Although several studies have been performed to establish the influence of polymerization conditions on the structure of the synthesized copolymer, they all involved 4th generation of Z-N catalyst [1,6,8].

In this study, the 5th generation of Ziegler-Natta catalyst was used and the effect of some polymerization conditions such as prepolymerization, external electron donor and monomer feed ratios was studied.

THEORY

Sequential Copolymerization Technique

To achieve a polymer structure in which a dispersed phase is regularly distributed inside the semi-crystalline homopolymer matrix, sequential polymerization of propylene is usually carried out in the first step, which is followed by ethylene/propylene copolymerization in the second step. A propylene homopolymer or a slightly modified copolymer is synthesized in the first step. In the second step, a mixture of ethylene and propylene is copolymerized with the same catalyst system, for obtaining a heterophasic system consisting of a microcrystalline matrix with a nearly amorphous elastomeric component dispersed within it. Homopolymerization of propylene with supported Z-N catalysts can be carried out in gas or liquid phase. The best EPR to provide impact per-

formance to a polymer is an amorphous, but it is highly soluble in diluents or liquid monomer, and hydrocarbons are highly soluble in the rubber. Thus, the only economically feasible way to add EPR to a homopolymer matrix is copolymerization in gas phase, following the homopolymer production stage [1].

Morphological Aspect

To produce a heterophasic copolymer, a proper amount of rubber must be produced in the copolymerization step, and furthermore the rubber must be retained inside the granule and homogeneously dispersed in the homopolymer matrix to prevent undesired reactor fouling. Thus, the catalyst porosity has to be carefully tailored. A high porosity (high pore volume) is required to bear the desired amount of rubber inside the particle and prevent its migration to the surface with a consequence reactor fouling [9,10].

In sequential copolymerization both inner and surface homopolymer porosities must be sufficiently high in order to bear the rubber internally and to preserve an adequately rough surface to avoid large interparticle friction due to rubber-rubber sticking [11-13].

Based on proposed models to describe the growth of polypropylene over $MgCl_2$ supported Z-N catalysts, such as Double Grain's model, polymer grain tends to reproduce both the shape, the dual structural hierarchy and porosity of the parent catalyst grain, enlarging the course its size as polymerization yield increases [14].

Structure of Polypropylene In-situ Blends

It is confirmed that in-situ polypropylene/poly(ethylene-co-propylene) blends are mainly composed of three parts: ethylene/propylene random copolymer, block copolymers with different lengths of ethylene and propylene segments and isotactic polypropylene. It has been considered that the block copolymer functions as compatibilizer between iPP and EPR phases, resulting in improvement of mechanical properties and random copolymer improves low temperature impact strength [15,16]. The relative amount of various components of PP alloy can be controlled or changed by the adjustment of various operational parameters such as polymerization time and monomer feed ratio.

EXPERIMENTAL

Materials

The 5th generation of spherical $MgCl_2$ supported Ziegler-Natta catalyst supplied by Basell Polyolefin's Co. containing 3.6 wt% Ti and 1,3-diether as internal donor was used. Triethylaluminium (TEA of 98% purity) from Fluka diluted in *n*-hexane was used as cocatalyst and the so-called D-donor (dicyclopentylidimethoxy silane) supplied from Basell Polyolefin's Co. was used as external electron donor (De). Polymer grade propylene was provided from Tabriz Petrochemical's and was used as received. Ethylene, hydrogen and nitrogen used were of >99.999% purity. Nitrogen and ethylene was further purified by passing over beds of absorbents.

Experimental Set-up

In this study, bulk (liquid monomer) homopolymerization was chosen concerning its similarity to the most industrial Natural Petrochemical Company processes (Spheripol, BP). Gas phase polymerization was the only option to gain amorphous EPR in the second stage of polymerization.

Polymerization reactor was a 1 L stainless steel vessel manufactured by Buchi Co. Since polymerization consisted of two different stages in series, liquid pool and gas phase, polymerization set-up was designed in order to conduct both liquid and gas-phase polymerization in one vessel. A schematic diagram of polymerization set-up is shown in Figure 1.

A high pressure N_2 line was used to transfer liquid monomer and catalytic system into the reactor.

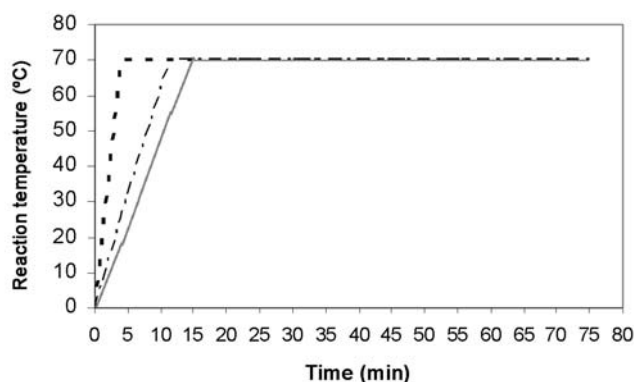


Figure 1. Reaction temperature profiles of three different non-isothermal prepolymerizations.

Catalyst system was injected to the reactor through a stainless steel cylinder under N_2 atmosphere. All gases were first purified online by passing through three purification trains (containing 13Å, 4Å, 3Å molecular sieves) in series. The individual gases were then filtered and flow of each reactant was measured and controlled with a Mass Flow Controller manufactured by Brooks.

Polymerization Procedure

A typical polymerization procedure was consisting of reactor preparation, homopolymerization (including prepolymerization and main polymerization) and copolymerization. Details are as follows:

Reactor Preparation

After washing the reactor with dry *n*-heptane, it was flushed with pure nitrogen at the wall temperature of about 90°C. Then reactor was evacuated for about 10 min and this procedure was repeated 5 times. Afterwards the reactor temperature was reduced to the desired initial reaction temperature.

Homopolymerization

Prescribed amount of hydrogen to control homopolymer molecular weight was injected to the reactor with a hydrogen press flow controller. Then, 600 mL of liquid propylene was introduced into the reactor under N_2 pressure. The desired amounts of diluted TEA and external donor (Al/De= 20 wt%) in *n*-hexane were precontacted under a nitrogen atmosphere at room temperature for 5 min. TEA/donor/*n*-hexane mixture was injected to the reactor through the high pressure cylinder under N_2 pressure. A quantity of 2-7 mg solid, non-activated catalyst was measured and suspended in some *n*-hexane in a vial and then injected to the reactor through the same high pressure cylinder. The cylinder was washed with fresh *n*-hexane to ensure that all catalyst is introduced. Catalyst injection temperature was adjusted to prepolymerization starting temperature. Then reaction temperature was raised to 70°C (main polymerization temperature) during specified prepolymerization time and kept at this temperature. Reaction time was recorded as the reaction temperature reached the main polymerization temperature. After the prescribed polymerization time, typically being 60 min, homopolymerization

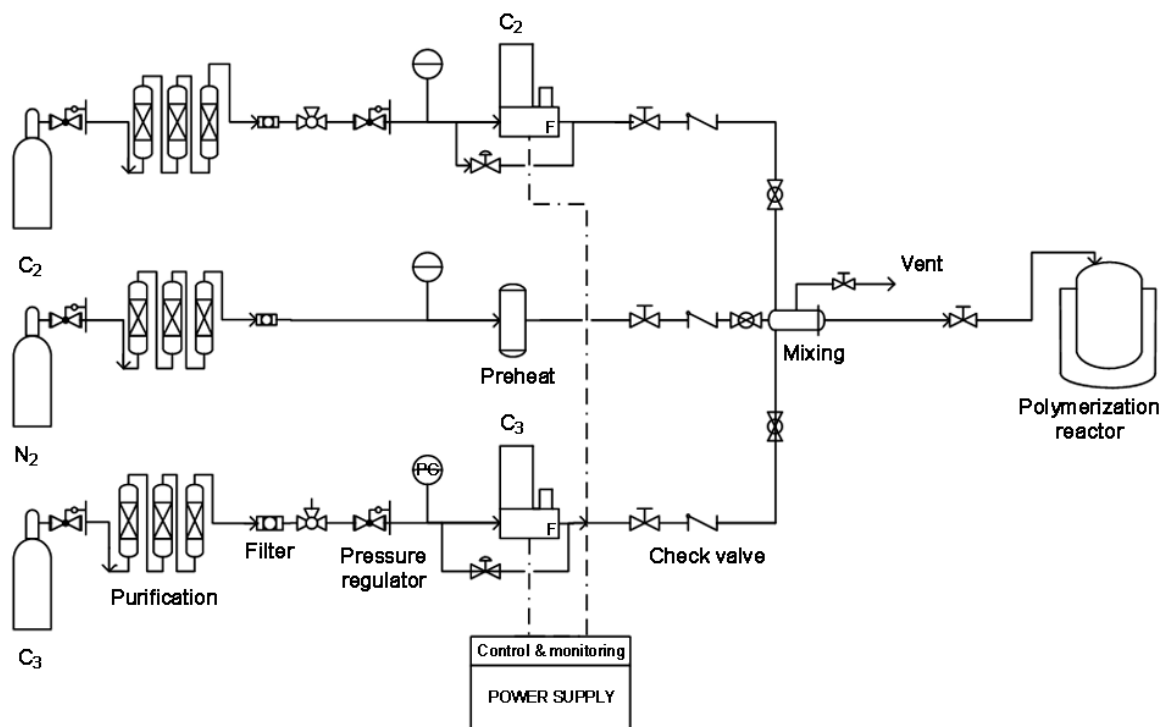


Figure 2. Schematic diagram of purification and injection unit of gaseous feeds.

reaction was stopped by opening the vent valve, allowing the non-reacted monomer to evaporate quickly.

Copolymerization

In this step, a prescribed amount of hydrogen to control copolymer MW was injected to the reactor. The mixture of ethylene and propylene (in gas phase) with constant molar ratio introduced to the reactor. Then reactor temperature was raised to 70°C. Copolymerization reaction was carried out at 70°C and 8 bar. Reaction carried out up to 2 h. In some cases, it was continued whilst the monomers consumption was reached the desired amount of rubber in the blend (about 15 wt%).

Polymer Characterization

Measurement of Homopolymer Isotacticity Index (II)

Isotacticity index of homopolymer was determined as a measure of non-soluble fraction of homopolymer in boiling *n*-heptane. 5 Grams of homopolymer samples were subjected to Soxhlet extraction with *n*-heptane for at least 24 h to remove the weakly tactic fraction. The weight percentage of non-soluble part was used as a measure of the content of isotactic polymer.

Measurement of Ethylene Content in the Blend

FTIR Spectra of the blend samples were recorded on a calibrated Bruker 55 Equinox FTIR spectrometer. A thin film of the sample was prepared through hot pressing.

Xylene Fractionation

The samples were dissolved in xylene at 135°C with reflux for 1 h. After this step the solution was gradually cooled to room temperature. The insoluble fraction at 25°C was separated by filtration and identified as crystalline polymer. The soluble phase at 25°C was precipitated from the solution in an acetone-methanol mixture and the amorphous polymer was separated. Oligomers remained soluble in the solvent mixtures [17].

RESULTS AND DISCUSSION

Polymer Morphology

Effect of Prepolymerization Time

Effect of prepolymerization time on particles morphology was studied. A non-isothermal prepolymerization, according to the method proposed by Pater

Table 1. Changes in EPR content in copolymer with different prepolymerization times.

Run	Prepolymerization time (min)	Maximum EPR content
1	4	15
2	6	12
3	8	8
4	12	6.2
5	15	5

Gas phase polymerization conditions: T: 70°C, P: 8 bar, time: 1 h, H₂: 0.02 mol, C₂/C₃= 0.78 mol%.

et al. [18], was carried out immediately after the catalyst injection. Pater showed that a short prepolymerization, lasting no longer than 10 min at an increasing polymerization temperature or polymerization rate is often sufficient to obtain perfect replication of the catalyst particle shape and morphology.

In order to study the effect of prepolymerization time on the shape of particles and catalyst performance in copolymerization stage, we carried out a number of runs with different prepolymerization times, (Figure 2). Catalyst injection temperature and polymerization were set to 25°C and 70°C, respectively.

Homopolymerization was carried out for 1 h at 70°C and copolymerization was conducted at the

ethylene/propylene ratio of 0.75 for 2 h. The final product after two stages of reaction was still free flowing, spherical granules. This means that in all cases the replication was took place, properly. The amount of EPR in each sample was measured by amorphous phase extraction. Results are shown in Table 1. Results showed that for the catalytic system used, increasing prepolymerization duration leads to decrease in the proportion of copolymer in the in-situ blend. Pater et al. [19] showed that in propylene polymerization using supported Z-N catalysts, with increasing polymerization temperature, bulk densities of the produced powders have rapidly decreased from the maximum value of about 450 g/L, to the lowest value around 350 g/L. Thus, the initial polymerization rate has to be carefully controlled to obtain fully replication of catalyst shape and porosity.

It can be concluded that reducing prepolymerization time could cause an increase in the average prepolymerization temperature, leading to increase in the rate of prepolymerization reaction. Consequently, homopolymer porosity is increased by reducing prepolymerization time, leading to maintain greater amount of rubber internally.

Characterization of a Selected In-situ Blend Structure

Because of the non-living nature of coordination polymerization, the PP/EPR in-situ alloy has a com-

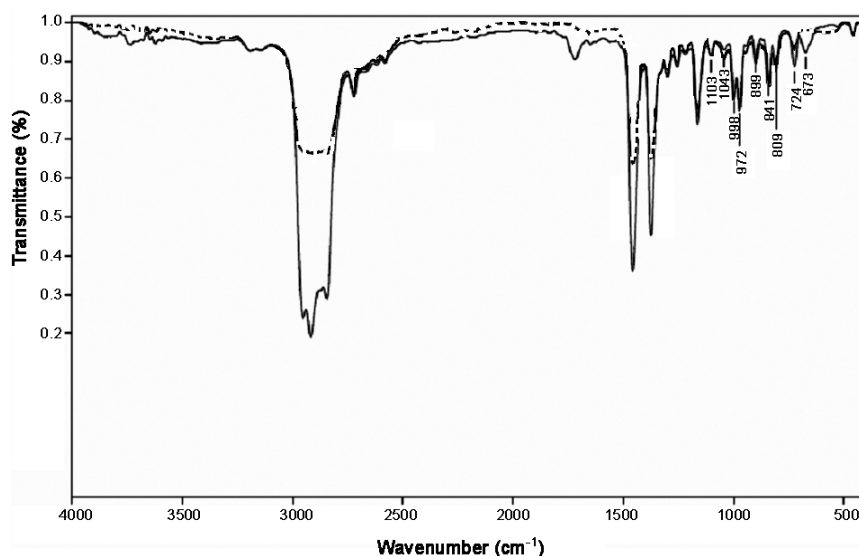


Figure 3. FTIR Spectra of synthesized in-situ blend (dotted line) and a reference sample (filled line).

plicated microstructure. Ethylene/propylene random copolymers, block copolymers with different chain lengths of ethylene and propylene, and propylene homopolymer can coexist in the PP/EPR in-situ alloy [20]. It has been considered that the block copolymers may function as compatibilizer between the iPP and EPR phase, resulting in improvement of mechanical properties. The microstructure of the PP/EPR in-situ alloy, for example, the weight percentage of various components and the composition of the components, has a great influence on its ultimate application and processing properties [21].

Rough investigation of the microstructure of the in-situ blend samples was carried out by FTIR. Figure 3 shows the spectra of a synthesized in-situ blend (dotted line) in comparison with the spectra of a reference sample- Moplen E 540V- supplied from Basell Polyolefin's Co. (filled line). Specifications of Moplen sample are mentioned in the appendix.

It can be observed that the doublet at 720-740 cm^{-1} is present in both samples, meaning that both contain ethylene/propylene random copolymers and crystalline PE chains or segments. The bands at 998 cm^{-1} and 841 cm^{-1} , which present long PP segments that can crystallize, are also present in both samples.

Influence of External Electron Donor on Catalyst Behaviour and Polymer Structure

To study the effect of external electron donor on catalyst behaviour in homopolymerization and copolymerization stages, 5 polymerization runs were carried out in the absence and presence of external electron donor. First, only homopolymerization runs were carried out in the presence and absence of electron donor and catalyst productivity in addition to polymer isotacticity investigated. Then multi-stages polymerizations in the presence and absence of external donor were carried out to obtain in-situ blend. Rate-time profile curves at copolymerization stages were recorded and produced polymers were fractionated to crystalline and amorphous fractions. The amount of ethylene in crystalline and amorphous phases was measured and compared. Results are as follows:

(a) Homopolymerization Stage

The effect of external electron donor on homopolymer isotacticity and catalyst productivity is shown in Table

Table 2. Effect of external electron donor on catalyst productivity and stereospecificity.

TEAL/donor (molar ratio)	Yield (kg PP/g cat.h)	Isotacticity index
No donor	20.0	96.8
15	15	97.5
20	14	97.8
30	9.25	98
40	5	98.5

Polymerization in liquid monomer, T: 70°C, time: 1 h, H₂: 0.12 mol.

2. As it is observed in this table, for the 5th generation of Z-N catalysts, using external electron donor reduces the catalyst productivity, although homopolymer isotacticity is slightly increased. This is in agreement with Cecchin's observations which showed that using external electron donor in conjunction with a 5th generation of Z-N catalyst caused both polymerization yield and catalyst hydrogen response to decrease [9]. Furthermore, the effect of external electron donor on the hydrogen response of the catalyst was studied. Results are shown in Table 3. As it can be observed from this table, external electron donor induced a decrease in the catalyst hydrogen response. In propylene polymerization, the reactivity of dormant sites (after 2,1 insertions) can be substantially higher with molecules smaller than propylene. In particular, the much higher insertion rate of hydrogen and ethylene vs. propylene into M-CH(CH₃)-CH₂-P (after 2,1 insertions) is proved [1]. Chadwick et al. [20] showed that in the polymer obtained with 1,3-diether containing catalysts, the distribution of the 2,1 units is narrow and even the most stereoregular fraction contains almost two regioirregular enchainments out of 1000. Therefore, H₂ finds more points of preferential attack (after 2,1 last inserted units) in the growing

Table 3. Effect of external electron donor on homopolymer MFI.

TEAL /donor (molar ratio)	H ₂ (mol)	Yield (kg PP/g cat.h)	MFI (g/10 min)
No donor	0.112	19	170
20	0.112	12.3	25
No donor	0.13	27	300
20	0.13	13	170

Polymerization in liquid monomer, T: 70°C, time: 1 h.

chain [21]. If we relate the catalyst hydrogen response to its regioselectivity, we can conclude that although external electron donor promoted catalyst stereoselectivity slightly, its main effect was, however, on the catalyst regioselectivity by which the catalyst hydrogen response was decreased.

(b) Copolymerization Stage

Figure 4 shows monomers consumption during copolymerization in the presence and absence of external electron donor. It can be concluded that addition of external electron donor changed the kinetic behaviour of the catalyst. As it can be observed from Figure 4, external electron donor reduced the rate of copolymerization. To study the effect of electron donor on copolymer molecular weight, we carried out 2 runs with similar conditions in the absence and presence of electron donor. Hydrogen in the first stage was adjusted to reach an MFI of 170 for homopolymer, so the changes in the blend MFI are related to changes in copolymer MW. It is noticeable that the external electron donor produced a heterophasic copolymer with lower MW (MFI is increased from 100 g/10 min to 200 g/10 min). Kissin et al. [22] have studied the kinetics of ethylene/1-hexene copolymerization reaction with a heterogeneous Z-N catalyst. He showed that addition of silane as external electron

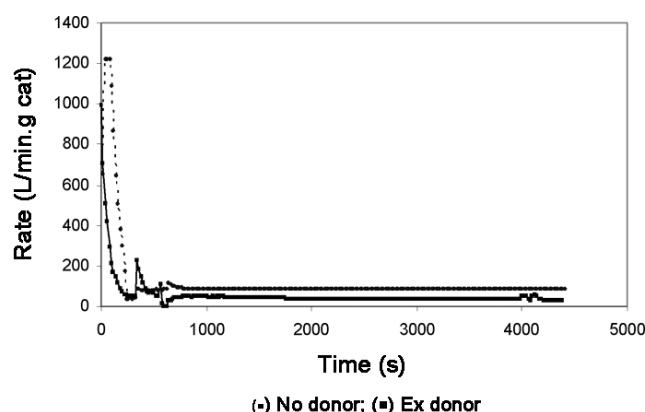


Figure 4. Effect of external donor on the rate of copolymerization, copolymerization conditions: T: 70°C, P: 8 bar, H₂: 0.02 mol, time: 2 h.

donor led to a progressive decrease in catalyst activity and increase in molecular weight.

The amount of ethylene in xylene soluble and non-soluble fractions of both copolymers was measured using FTIR. Results are shown in Table 4. This table indicates that in the case of catalytic system used, external electron donor gives rise to an increase in the ratio of amorphous to crystalline ethylene/propylene copolymer. It can be also concluded that the external electron donor decreases the amount of ethylene in both amorphous and crystalline ethylene/propylene

Table 4. Effect of external electron donor on copolymer specifications.

TEAL/donor (molar ratio)	Xylene soluble (wt%)	MFI (g/10 min)		C ₂ - (wt%)		Amorphous/ crystalline copolymer (wt%)
		Homopolymer	In-situ blend	Xylene insoluble fraction	Xylene soluble fraction	
No donor	22	170	>200	6	42	74
20	12.5	170	87	2.7	34.3	92

Polymerization conditions: first stage: liquid monomer, T: 70°C, time: 1 h, H₂: 0.12 mol, second stage: C₂/C₃: 0.82 mol%, H₂: 0.02 mol, P: 8 bar, time: 2 h.

Table 5. Changes in EPR content in copolymer with ethylene/propylene ratio.

Run	Xylene soluble (wt%)	Ethylene/propylene (mol%)	C ₂ in Xylene insoluble (wt%)
1	12.6	82	2.7
2	13.5	87	3
3	14.2	100	3.3

Gas phase polymerization conditions: T: 70°C, P: 8 bar, H₂: 0.02 mol, time: 2 h, (TEAL/donor: 20 mol%)

copolymer.

It is generally believed that in a heterogeneous Ti-based Ziegler-Natta catalyst, a spectrum of active sites exists which may have different r_1r_2 products.

The differences in the r_1r_2 behaviours of the amorphous versus the crystalline ethylene/propylene copolymers can reveal information about the types of catalyst sites that produced two different ethylene/propylene copolymer components. The amorphous ethylene/propylene has r_1r_2 products close to unity, which is only possible for narrow compositional distributions and random sequence distributions. This suggests a singular type of catalyst site.

The much higher r_1r_2 for the crystalline ethylene/propylene copolymers suggests a broad range of ethylene contents, which originate from a different type or a different family of catalyst sites [23]. Randall [23] used 4th generation of Z-N catalyst in two-stage polymerization at different polymerization conditions. He showed that the distribution of amorphous versus crystalline copolymers remains constant over a broad total ethylene range and different copolymer levels. This behaviour suggests that the distribution of these two ethylene/propylene copolymer components reflects the corresponding distribution in population between two basic types of catalyst sites. Evidence was also obtained in his study that, the sites producing the crystalline ethylene/propylene copolymers are sensitive toward the choice of electron donor for the catalyst system. The amount of crystalline ethylene/propylene copolymers relative to the amorphous ethylene/propylene copolymers can be reduced by selecting catalyst donors that increase the stereoregularity of iPP homopolymers. An analogous situation exists for iPP homopolymer component. Increasing stereoregularity through increasing electron donor concentrations leads to a reduced amount of the symmetric chain components [20]. It can be concluded that external electron donor makes the portion of active centres responsible for producing crystalline ethylene/propylene (have r_1r_2 products greater than unity) to decrease.

Effect of Ethylene/Propylene Ratio on the Rate of Copolymerization

Three runs with different ethylene/propylene ratios at similar copolymerization duration were carried out

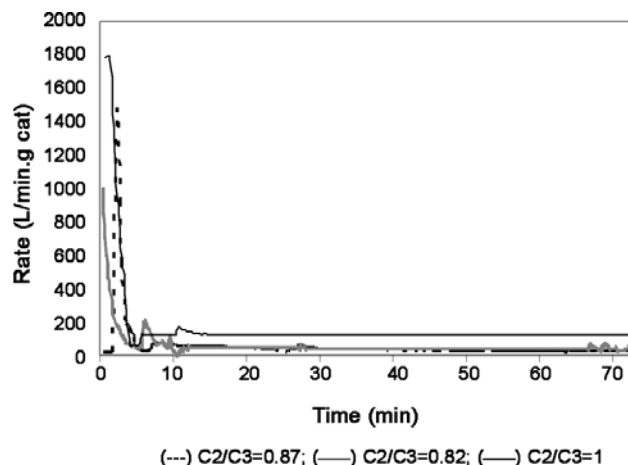


Figure 5. Effect of ethylene/propylene ratio on the rate of copolymerization, copolymerization conditions: T: 70°C, P: 8 bar, H₂: 0.02 mol, time: 2 h.

and the rate of polymerization in the second stage was compared (Figure 5). As it can be observed in Figure 5, the polymerization rate increases with increasing C₂/C₃ ratio. This can be due to the higher reactivity of ethylene toward propylene because of its lower steric hindrance around the double bond [24]. The amount of EPR in each sample is measured by amorphous phase extraction. The results are shown in Table 5, which show that increasing ethylene/propylene ratio leads to increase in the proportion of EPR in the in-situ blend.

CONCLUSION

A method using a single polymerization reactor to synthesize in-situ blends containing up to 15 wt% rubbery phase is proposed. It was demonstrated that to obtain proper homopolymer porosity, using a non-isothermal prepolymerization step (about 4 min) could be a good option at the early stages of homopolymerization. For the catalytic system used, external electron donor lowers the catalyst productivity and hydrogen response. A lower catalyst hydrogen response while using external electron donor may be attributed to the enhancement of catalyst regioselectivity. The results obtained from fractionation of copolymer into crystalline and amorphous phase revealed that external electron donor reduces the ratio

of crystalline to amorphous copolymer. This can be due to the changes occurring in the ratio between two basic types of catalyst sites responsible for producing crystalline and amorphous phases. As a matter of fact the amount of crystalline ethylene/propylene copolymers relative to the amorphous ethylene/propylene copolymers can be reduced by external electron donor that increases the stereo and regioregularity of the isotactic polypropylene homopolymers.

ACKNOWLEDGEMENTS

The work presented in this article was carried out in cooperation with Basell Polyolefin's Co. and the National Petrochemical Company (R&T). The authors wish to thank NPC R&T for the financial and Basell Polyolefin's Co. for the intellectual input.

REFERENCES

1. Moore E.P., *Polypropylene Handbook*, Pasquini N. (Ed.), 2nd ed., Hanser, Munich, Ch. 5, 2005.
2. Kocsis J.K., *Polypropylene, Structure, Blends and Composites*, 1st ed., Chapman & Hall, London, 2, Ch. 1, 1995.
3. Moore E.P., *The Rebirth of Polypropylene*, Hanser, Munich, Ch. 9, 1998.
4. Galli P., Vecellio G., Technology, driving force behind innovation and growth of polyolefins, *Prog. Polym. Sci.*, **26**, 1287-1336, 2001.
5. Galli P., Forty years of industrial developments in the field of isotactic polyolefins, *Macromol. Symp.*, **89**, 13-26, 1995.
6. Zhang Y.Q., Fan Zhi Q., Feng Lin X., Influence of copolymerization conditions on the structure and properties of reactor blends of polypropylene/ethylene-propylene, *J. Appl. Polym. Sci.*, **84**, 445-453, 2002.
7. Polypropylene for thin wall packaging, <http://www.borealis.com/packaging/thin wall>.
8. Penzo G., Process technology: Evolution and revolution, polypropylene, past, present and future, *Proc. 1st Anniversary of the PP Symp.*, Ferrara, Montell Italia, Ferrara, 75-100, 1998.
9. Cecchin G., Morrini U., On the mechanism of polypropylene growth over $MgCl_2/TiCl_4$ catalyst system, *Macromol. Chem. Phys.*, **202**, 1987-1994, 2001.
10. Debling J.A., Ray W.H., Morphological development of impact polypropylene produced in gas phase with a $TiCl_4/MgCl_2$ catalyst, *J. Appl. Polym. Sci.*, **81**, 3085-3106, 2001.
11. Ven S.V.D., *Polypropylene and Other Polyolefins*, Elsevier Science, Ch. 5, 1990.
12. Cecchin G., Morrini U., Polypropylene product innovation by reactor granule technology, *Macromol. Symp.*, **173**, 195-209, 2001.
13. Weickert G., Meier G.B., Pater J.T.M., Westerterp K.R., The particles as microreactor: Catalytic propylene polymerization with supported metallocenes and Z-N catalysts, *Chem. Eng. Sci.*, **54**, 3291-3296, 1999.
14. Kakugo M., Sadatoshi H., Sakai J., Growth of polypropylene particles in heterogeneous Ziegler-Natta polymerization, *Macromolecules*, **22**, 3172-3177, 1989.
15. Xu J.T., Fu Z.S., Wang X.P., Geng J.S., Fan Z.Q., Effect of the structure on the morphology and spherulitic growth kinetics of polyolefin in-reactor alloys, *J. Appl. Polym. Sci.*, **98**, 208-215, 2005.
16. Xu J., Feng L., Characterization of microstructure of polypropylene alloys, *Polym. Int.*, **47**, 433-438, 1998.
17. Pires M., Mauler R., Liberman S., Structural characterization of reactor blends of polypropylene and ethylene-propylene rubber, *J. Appl. Polym. Sci.*, **92**, 2155- 2162, 2004.
18. Pater J.T.M., Weickert G., Van Swaaij W., Polymerization of liquid propylene with a fourth-generation Z-N catalyst: Influence of temperature, hydrogen, and prepolymerization method on powder morphology, *J. Appl. Polym. Sci.*, **87**, 1421-1435, 2002.
19. Pater J.T.M., Weickert G., Van Swaaij W., Polymerization of liquid propylene with a fourth-generation Z-N catalyst: Influence of temperature, hydrogen, and prepolymerization method on polymerization kinetics, *Chem. Eng. Sci.*, **57**, 3461-3477, 2002.
20. Chadwick J.C., Busico V., Influence of Ziegler-Natta catalyst regioselectivity on polypropylene

- MWD and rheological and crystallization behavior, *Macromolecules*, **37**, 9722-9727, 2004.
21. Busico V., Chadwick J.C., Propene/ethylene- ^{13}C copolymerization as a tool for investigating catalyst regioselectivity. MgCl_2 /internal donor/ TiCl_4 -external donor/ AlR_3 system, *Macromolecules*, **37**, 7437-7443, 2004.
 22. Kissin Y., Rishina L., Hydrogen effects in propylene polymerization reactions with titanium-based Ziegler-Natta catalysts. I. Chemical mechanism of catalyst activation, *J. Appl. Polym. Sci. Part A*, **40**, 1353-1365, 2002.
 23. Randall J.C., Sequence distribution versus catalyst site behavior of in-situ blends of polypropylene and poly(ethylene-co-propylene), *J. Polym. Sci. Part A*, **36**, 1527-1542, 1998.
 24. Kissin Y.V., *Transition Metal Catalyzed, Polymerizations: Alkenes and Dienes*, Quirk P. (Ed.), Harwood Academic, New York, Part B, 597, 1983.